UNIVERSITI PUTRA MALAYSIA

THE EFFECTS OF DOPANTS ON THE PHYSICO-CHEMICAL PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS

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By

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THE EFFECTS OF DOPANTS ON THE PHYSICO-CHEMICAL PROPERTIES OF VANADYL PYROPHOSPHATE CATALYSTS

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November 2003

Chairman: **Associate Professor Taufiq Yap Yun Hin, Ph.D.**

Faculty: **Science and Environmental Studies**

Vanadium phosphorus oxide (VPO), is a commercial catalyst for selective oxidation of butane to maleic anhydride. The nature of the oxidant of the doped and undoped $(VO)_2P_2O_7$ catalysts derived from (i) VPO, reaction of V_2O_5 with H_3PO_4 in isobutanol and (ii) VPD, reaction of $VOPO_4 \cdot 2H_2O$ with isobutanol were investigated. Metal cations, namely of sodium, potassium, magnesium and bismuth, were added as dopants into $(VO)_2P_2O_7$ lattice.

From the Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) analysis, the catalysts which have gone through a series of redox reaction do not produce the original morphology of $(VO)_2P_2O_7$.

The results indicated that the addition of dopants lowered the Brunauer-Emmet-Teller (BET) surface area of vanadyl pyrophosphate catalysts, except Bi-doped VPD catalysts. All the doped VPO and VPD catalysts have been shown a vanadyl pyrophosphate phase with three distinct peaks at 22.9°, 28.4° and 29.3° in X-ray Diffraction (XRD) analysis. The Bi-doped VPO and VPD catalysts had significantly

shifted the first reduction peak to a lower temperature in H_2-TPR analysis. The introduction of Bi have modified the $(VO)_2P_2O_7$ matrix and mobility of these catalyst increased. It can be seen from TPRn analysis where VPDBi1 increased the selectivity of butene and butadiene (selective products) and decreased the selectivity of CO and CO_2 (unselective products).

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

KESAN DOPANT TERHADAP PENCIRIAN FIZIKO-KIMIA MANGKIN VANADIL PIROFOSFAT

Oleh

TAN KIAN PENG

November 2003

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Vanadium fosforus oksida (VPO), adalah mangkin komersial untuk pengoksidaan selektif butana kepada maleik anhidrida. Sifat pengoksidaan bagi mangkin $(VO)_2P_2O_7$ yang dimodifikasi dan tidak dimodifikasi disediakan melalui (i) VPO, tindak balas V_2O_5 dengan H_3PO_4 dalam isobutanol dan (ii) VPD, tindak balas $VOPO_4 \cdot 2H_2O$ dengan isobutanol telah dikaji. Kation logam, seperti natrium, kalium, magnesium and bismuth telah ditambahkan sebagai dopant dalam kekisi $(VO)_2P_2O_7$.

Daripada analisis mikroskop elektron imbasan (SEM) and mikroskop elektron transmisi (TEM), mangkin di mana telah melalui satu siri keadaan tindakan redoks tidak lagi menghasilkan morfologi $(VO)_2P_2O_7$ yang asal.

Keputusan menunjukkan bahawa penambahan dopant telah menurunkan luas permukaan Brunauer-Emmet-Teller (BET) bagi mangkin vanadil pirofosfat kecuali mangkin VPD yang dimodifikasi dengan Bi. Semua mangkin VPO dan VPD yang dimodifikasi menunjukkan fasa vanadil pirofosfat dengan tiga puncak ketara iaitu 22.9°, 28.4° and 29.3° dalam pembelauan sinar-X (XRD). Mangkin VPO dan VPD

yang dimodifikasi dengan Bi telah mengalihkan puncak penurunan pertama kepada suhu yang lebih rendah secara ketara dalam analisis H_2-TPR. Kehadiran Bi telah memodifikasikan matriks $(VO)_2P_2O_7$ dan menambahkan mobiliti mangkin tersebut. Ini dapat dilihat daripada analisis TPRn di mana VPDBi1 telah meningkatkan selektiviti butena dan butadiena (produk selektif) dan mengurangkan selektiviti CO dan CO_2 (produk tidak selektif).

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I certify that an Examination Committee met on 19th November 2003 to conduct the final examination of Tan Kian Peng on his Doctor of Philosophy thesis entitled "The Effects of Dopants on the Physico-Chemical Properties of Vanadyl Pyrophosphete Catalysts" in accordance with Universiti Pertanian Malaysia (Higher Degree) Act 1980 and Universiti Pertanian Malaysia (Higher Degree) Regulations 1981. The Committee recommends that the candidate be awarded the relevant degree. Members of the Examination Committee are as follows:

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DECLARATION

I hereby declare that the thesis is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UPM or other institutions.

TAN KIAN PENG

Date: 26 / 2 / 2004

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LIST OF ABBREVIATIONS

ASAP	Analysis of Surface Area and Porosity
BET	Brunauer-Emmet-Teller
CCD	Charge Coupled Device
EPA	Environmental Protection Agency
FID	Flame Ionization Detector
FWHM	Full Width of Half Maximum
ICP-AES	Inductively Coupled Plasma-Absorption Emission Spectroscopy
JEOL	Japan Electron Optics Laboratory
IUPAC	International Union of Pure and Applied Chemistry
JCPDS	Joint Committee Powder Diffraction Standards
MA	Maleic Anhydride
MS	Mass Spectrometer
TCD	Thermal Conductivity Detector
THF	Tetrahydrofuran
SEM	Scanning Electron Microscopy
TEM	Transmission Electron Microscopy
TPD	Temperature Programmed Desorption
TPO	Temperature Programmed Oxidation
TPR	Temperature Programmed Reduction
TPRn	Temperature Programmed Reaction
XRD	X-ray Diffraction

CHAPTER 1

INTRODUCTION

1.1 Definition of Catalysis and Catalyst

Although nowadays catalytic processes have already been applied for a long period of time, it was not until 1836 that Berzelius introduced the term 'catalysis' (Bond, 1987). The word catalysis comes from two Greek words, the prefix *cata-*, meaning down, and the verb *lysein*, meaning to split or break. By `awaking affinities which are asleep', a catalyst breaks down the normal forces which inhibit the reactions of molecules.

Later, in 1895, William Ostwald was the first to write down a definition of a catalyst: 'A catalyst is a substance that change the rate of a chemical reaction without itself appearing in the products'. A material scientist might describe a catalyst as a device for chemical transformation (Gates, 1995): Reactant molecules flow into the device and are transformed into product molecules that flow out; energy may be consumed or liberated. It is important to note that a catalyst does not influence the thermodynamic equilibrium of reactants and products. Therefore, the current definition is slightly better, though close to Ostwald's description: 'A catalyst is a substance that increases the rate of approach to thermodynamic equilibrium of a chemical reaction without being substantially consumed'.

Catalysts are among the most important technological materials, being used in the manufacture of chemicals, fuels, foods, clothing, pharmaceuticals, and materials such as organic polymers (Gates, 1992). The value of the goods manufactured in the United States in processes that at some stage involve catalysis is about $1 trillion annually; the catalysts used in these processes cost only a few tenths of a percent of the value of the products.

The solid catalysts are far more important than the others in large-scale processes for conversion of chemicals, fuels, and pollutants (Satterfield, 1991). Many solid elements and compounds, including metals, metal oxides, and metal sulfides, are catalysts. A few industrial catalysts are simple in composition, for example, Raney nickel, used for hydrogenation of fats, and γ -Al_2O_3, used for dehydration of ethanol to make ethylene. However, the typical industrial catalyst consists of a variety of components and phases and is so complex that the structure is not well understood.

The activity of a catalyst is a measure of how fast it catalyses a reaction. The selectivity is a measure of how well the catalyst directs the conversion to desired products; a highly selective catalyst is much more active for the desired reactions. The stability of a catalyst is a measure of how fast it loses activity or selectivity in operation. The regenerability is a measure of how effectively a deactivated catalyst can be brought back to a state of high activity and selectivity (Gates, 1995).

1.1.1 Classification of Catalytic Systems

In fact, it is possible to divide catalytic systems into two distinct categories (Bond, 1987). When the catalyst is of the same phase as the reactants and no phase boundary exists, it is a homogeneous catalysis. This may take place either:

(i) in the gas phase, as, for example, when nitrogen oxide catalyses the oxidation of sulphur dioxide; or

(ii) in the liquid phase, as when acids and bases catalyse the mutarotation of glucose.

When a phase boundary separates the catalyst from the reactants, it is a heterogeneous catalysis. Catalysis is essentially a chemical phenomenon. The ability of a substance to act as a catalyst in a specified system depends on its chemical nature. Heterogeneous catalysis are concerned with the specific chemical properties of the surface of the chosen substance. These of course reflect the chemistry of the bulk solid, and some useful insight into the catalytic activities of surfaces is gained from knowledge of the bulk properties of the solid. Table 1.1 shows the classification of heterogeneous catalysts. For catalysis to occur, there must be a chemical interaction between catalyst and the reactant-product system, but this interaction must not change the chemical nature of the catalyst except at the surface.

Table 1.1: Classification of heterogeneous catalysts (less important functions in parentheses) (Bond, 1987)

Class	Functions	Examples
Metals	hydrogenation dehydrogenation hydrogenolysis (oxidation)	Fe, Ni, Pd, Pt, Ag
Semiconducting oxides and suphides	oxidation dehydrogenation desulphurization (hydrogenation)	NiO, ZnO, MnO_2, Cr_2O_3, Bi_2O_3-MoO_3, WS_2
Insulator oxides	dehydration	Al_2O_3, SiO_2, MgO
Acids	polymerization isomerization cracking alkylation	H_3PO_4, H_2SO_4, SiO_2-Al_2O_3, zeolites

1.1.2 Catalysts for Industrial Processes: General Requirements

The criteria for an industrially successful catalyst are very stringent. First, the catalyst must be able to effect the desired reaction at an acceptable rate under conditions of temperature and pressure that are practicable (Anderson, 1975). Chemical technology has advanced to the point where temperatures as high as 1600 K and pressures up to 350 atm (35 MPa). If however good yields can be obtained at low temperatures and pressures, then there is every incentive to find a catalyst that will operate under the mildest possible conditions, since the use of extreme conditions is very costly. It is

concurrently important that side-reactions are minimal, especially those leading to poisoning or deactivation through carbon deposition on catalyst.

Second, the catalyst must be able to sustain the desired reaction over prolonged periods: in some processes, a catalyst life of several years is not uncommon, and is economically necessary. Clearly the longer it lasts, the smaller will be the contribution that its initial cost makes to the overall cost of the process. Initial cost is rarely of over-riding importance: it is usually cheaper in the long run to use an expensive catalyst that will last a long time than a cheap one that has to be replaced frequently.

1.2 Catalytic Oxidation Processes

It was in the first decades of the 20^{th} century, however, that catalytic processes began to appear in significant numbers, though the first heterogeneously-catalysed process, the "contact process", had begun to render obsolescent the chamber process some twenty years earlier (Chinchen *et al.*, 1987). More than 60 % products by catalytic route in chemical industry are by oxidation and the world market for oxidation catalysts may be estimated as around 200-250 million US dollars, about half of which are in Europe (Centi, 1993a).

Many industrial catalytic direct oxidation processes have been successfully developed and introduced since the "contact" process, mainly with the objective of